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PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

To:

ANGLISS, Michael, L.
Davies Collison Cave
1 Little Collins Street
Melbourne, VIC 3000
AUSTRALIE

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

Date of mailing (day/month/year) 22 June 1999 (22.06.99)	
Applicant's or agent's file reference 2112337/MLA	**IMPORTANT NOTIFICATION**
International application No. PCT/AU98/00854	**International filing date** (day/month/year) 14 October 1998 (14.10.98)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
HUNTSMAN SURFACTANTS TECHNOLOGY CORPORATION 500 Huntsman Way Salt Lake City, UT United States of America	US	US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

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HUNTSMAN SURFACTANTS TECHNOLOGY CORPORATION 500 Huntsman Way Salt Lake City, UT 84108 United States of America		
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

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[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Peggy Steunenberg
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

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NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

ANGLISS, Michael, L.
Davies Collison Cave
1 Little Collins Street
Melbourne, VIC 3000
AUSTRALIE

Date of mailing (day/month/year) 22 April 1999 (22.04.99)	
Applicant's or agent's file reference 2112337/MLA	IMPORTANT NOTIFICATION
International application No. PCT/AU98/00854	International filing date (day/month/year) 14 October 1998 (14.10.98)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

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State of Nationality: AU
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Facsimile No.:
Teleprinter No.:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

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United States of America

State of Nationality: US
State of Residence: US
Telephone No.:
Facsimile No.:
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Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

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Date of mailing (day/month/year) 03 June 1999 (03.06.99)	
International application No. PCT/AU98/00854	**Applicant's or agent's file reference** 2112337/MLA
International filing date (day/month/year) 14 October 1998 (14.10.98)	**Priority date** (day/month/year) 14 October 1997 (14.10.97)
Applicant KIRBY, Andrew, Francis et al	

1. The designated Office is hereby notified of its election made:

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14 May 1999 (14.05.99)

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A1

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PO 9767 14 October 1997 (14.10.97) AU

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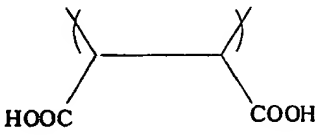
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: KIRBY, Andrew, Francis [AU/AU]; 20 Ann Street, Footscray, VIC 3011 (AU). PARR, Rodney, Walter [AU/AU]; 13 Wilma Court, Doncaster, VIC 3108 (AU). TUDOR, Phillip, Robert [AU/AU]; 5 Gordon Avenue, Elwood, VIC 3184 (AU). PARRIS, David, Hayshiv [AU/AU]; 6/2 Manningham Street, Parkville, VIC 3052 (AU).

(74) Agents: ANGLISS, Michael, L. et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).

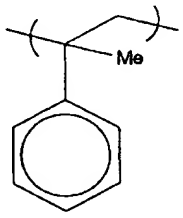
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD OF DISPERSING AN INSOLUBLE MATERIAL IN AQUEOUS SOLUTION AND AGRICULTURAL FORMULATION



(I)



(II)

(57) Abstract

A method of dispersing an insoluble material in an aqueous solution comprising the following steps: (I) providing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first commoner and at least one residue of a second commoner, wherein said first commoner comprises α,β–unsaturated oxyacids or anhydrides and said second commoner comprises olefinic compounds containing one or more polymerizable double bonds; and (II) dispersing said formulation in an aqueous medium.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 98/00854

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: A01N 25/30; B01F 17/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: A01N 25/30; B01F 17/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT: copolymer: or polymer: or resin:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No: 88-010725/02, Class A97, C03, JP 62-273901 A (KAO CORP) 28 November 1987 Abstract	1,4-6,24,31-37,42
X	Derwent Abstract Accession No: 84-111236/18, Class A82, G02, JP 59-051963 A (NIPPON ZEON KK) 26 March 1984 Abstract	1,5-7,12-16,19-21,56,60-63,67-69
X	Derwent Abstract Accession No: 93-005617/01, Class A97, E33, F09, G02 (A14, A82), JP 04-334535 A (TOSOH CORP) 20 November 1992 Abstract	1,5-7,12-15,56,60-62

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
23 November 1998	10 DEC 1998
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929	Authorized officer **GAYE HOROBIN** Telephone No.: (02) 6283 2069

Form PCT/ISA/210 (second sheet) (July 1998) copbko

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 98/00854

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No: 42445 E/21, Class A14 (A97), JP 57-063124 A (AGENCY OF IND SCI TECH) 16 April 1982 Abstract	1,5-7,12-15,56,60-63
X	Derwent Abstract Accession No: 65045D/36, Class A82, G02 (A18), JP 56-089829 A (KAO SOAP KK) 21 July 1981 Abstract	1,5-7,12-15,56,60-63
X	Derwent Abstract Accession No: 87094153/12, Class A97, C03, JP 62-036302 A (KUMIAI CHEM IND KK) 17 February 1987 Abstract	1,5-8,12-15, 17, 22, 24, 33-35, 37, 42, 43,56,60-63,65,70,71
X	FR 2545325 A (SEDAGRI) 9 November 1984 Whole document	1,5,6,8,14,15,22,24,28,32-35,42,62,63,70
X	US 4175066 A (SHIBAZAKI et al) 20 November 1979 Claims and Examples	1,4,7,12,14,15,56,60, 62
X	EP 398724 A (ROHM AND HAAS COMPANY) 22 November 1990 Pages 4, 5, Examples	1,4,5,6
X	EP 608845 A (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION) 3 August 1994 Page 5 lines 26-30, Examples, Claims	1,4-6
X	GB 1414964 A (ENGLISH CLAYS LOVERING POCHIN & COMPANY LTD) 19 November 1973 Page 2 lines 37-42, Examples	1,5,6
X	EP 592169 A (ROHM AND HAAS COMPANY) 13 April 1994 Page 2	1,5,6
X	GB 2087862 A (DEARBORN CHEMICALS LIMITED) 3 June 1982 Page 1 lines 54-60, Claims	1,5
X	US 5183574 A (HWA et al) 2 February 1993 Examples and Claims	1,5

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 98/00854

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
FR	2545325	NONE					
US	4175066	DE	2816381	FR	2387911	GB	1585448
		JP	53129200				
EP	398724	BR	9002161	CA	2015980	JP	3115314
		PT	94080	ZA	9003688	US	5360570
		US	5244988	DD	295168		
EP	608845	AU	53978/94	AU	52336/96	CA	2119998
		EP	869169	EP	875553	EP	878446
		EP	879793	JP	6315622	JP	9052040
GB	1414964	NONE					
EP	592169	AU	48785/93	CA	2107410	CN	1086233
		JP	6115930	NZ	248855		
GB	2087862	CA	1174936	DE	3145283	ES	507169
		ES	8301840	FR	2494130	GB	2087862
		IT	1144928	JP	57113897	SE	8106839
		US	4559156				
US	5783574	CA	2166617	EP	711296	WO	95/32208

END OF ANNEX

separate the active material in the presence of a salt of an acidic resin, such as, for example, a copolymer of maleic anhydride and an α-olefinic compound; add an organic solvent which forms, together with the aqueous medium, a two-phase system; treat such two-phase system by adding a carrier substance thereto; and then isolate the product by a reduction in the volume of the organic phase by the addition of water, the solvent gradually transferring into the added water.

We have now found that the use of a range of derivatisations of alternating copolymers of an α,β-unsaturated oxyacid and an olefin having one or more polymerizable double bonds provides improved dispersibilty and suspensibility in agrochemical formulations, compared to those dispersants already described in the prior art, as well as a number of other ancillary benefits which will be more fully described herein.

According to a first aspect of the present invention, there is provided a method of dispersing an insoluble material in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic

compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium.

According to a second aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

(iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

According to a third aspect of the present invention, there is provided a method of making

an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

According to a fourth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic

compounds containing one or more polymerizable double bonds; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

According to a fifth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

According to a sixth aspect of the present invention, there is provided a formulation produced by the process of the second, third, fourth and fifth aspects.

According to a seventh aspect of the present invention, there is provided an agricultural formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds.

According to an eighth aspect of the present invention, there is provided a method of treatment of a substrate with a insoluble material comprising the following steps:

(i) preparing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

(ii) dispersing said formulation in an aqueous medium; and

as obtained from ECOTERIC AS 20 and ECOTERIC AS10 (Orica Australia Pty Ltd). Most preferred from the monoalkylsulphosuccinate class are sodium or potassium salts of cyclohexyl, iso-octyl and n-octyl sulphosuccinate. Most preferred from the dialkylsulphosuccinate class are sodium or potassium salts of dicyclohexyl, diisooctyl and di-n-octyl sulphosuccinates. Most preferred from the class of nonionic surfactants loaded onto insoluble porous silicate carriers are ethoxylated surfactants loaded onto carriers such as TERIC 157 (Orica Australia Pty Ltd). Most preferred wetting agents from the urea surfactant complexes are urea adducts of alcohol ethoxylate surfactants such as TERWET 7050 (Orica Australia Pty Ltd). The wetters herein described show good wettability and dispersibility for the formulations and have the additional advantage of showing storage stability in combination with the copolymer dispersants described. Whereas by comparison some commonly used WG and WP wetters such as alkylnaphthalene sulphonate salts and lignosulphonate salts have been found to show poor storage stability.

In the case of SC formulations in the present invention an active ingredient is typically added to water containing a dispersant, preferably with a surfactant wetting agent together with a conventional non-ionic dispersant. A humectant may also be included. A dispersion is formed using high shear mixing. The dispersion is then milled by any one of several means of wet milling so that the mean particle size of the dispersed solid is below 5 μm more typically in the range of from 1 to 3μm. The resulting product is known as a millbase and may be modified with additives such as antifreeze, thickeners and antisettling agents, biocides and colouring agents may be added. For an SC formulation to be acceptable it should not

Example 3.

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Orica Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of an alternating copolymer of n-octene and maleic anhydride of approximate molecular weight 20,000 to 30,000. The granules were prepared and tested in the manner described in Example 1. The results are shown in TABLE 1.

Example 4.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a copolymer of n-decene and maleic anhydride. Results are shown in TABLE 1.

Example 5.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a copolymer of diisobutylene and maleic anhydride of approximate molecular weight 30,000 to 40,000. Results are shown in TABLE 1.

Example 6.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 1000 (Atochem Inc.) which is a 1:1 molar ratio copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

Example 7.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 3000 (Atochem Inc.) which is a 3:1 molar ratio copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

Example 8.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of GANTREZ AN 119 resin (Rhodia Inc.) which is a copolymer of methylvinyl ether and maleic anhydride. Results are shown in TABLE 1.

Example 9.

A Simazine 900g/kg WG formulation of the following composition was prepared.

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Orica Australia Pty Ltd)	1.5
DISPERSANT	6.2
Water	0.5%

The dispersant used was the monoammonium salt of an alternating copolymer of diisobutylene

and maleic anhydride. The granules were prepared and tested in the manner described in Example 1. Results are shown in TABLE 1.

Example 10

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Orica Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of an alternating copolymer of undecylenic acid and maleic anhydride. The granules were prepared and tested in the manner described in example1. Results are shown in TABLE 2.

Example 11

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating copolymer of vinyl isobutyl ether and maleic anhydride. Results are shown in TABLE 2.

Example 12

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating copolymer of

Atrazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Orica Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in Example 1. Results are shown in TABLE 2.

Example 22

An Atrazine 900g/kg WG formulation was prepared and tested in the manner described in Example 21 with the dispersant being the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 23

A Diuron 900g/kg WG formulation of the following composition was prepared.

Diuron tech. (97% w/w)	92.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 3050 by Orica Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	2.1
Water	0.5

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in example 1. Results are shown in TABLE 2.

Example 24

A Diuron 900g/kg WG formulation was prepared and tested in the manner described in example 23 with the dispersant being the sodium salt of an alternating co-polymer of alphamethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 25

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Orica Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of a terpolymer not of alternating character between comonomers of first and second type comprising alphamethylstyrene, styrene and maleic anhydride. The granules were prepared and tested in the manner described in example1. Results are shown in TABLE 2.

Example 26.

Atrazine tech. (98% w/w)	91.8	% w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 3050 by Orica Australia Pty Ltd)	1.5	
DISPERSANT	3.1	
Kaolin	3.1	
Water	0.5	

with the dispersant being the sodium salt of a terpolymer of alternating character between monomers of first and second type comprising alphamethyl styrene, dicyclopentadiene and maleic anhydride. The granules were made and tested as described in Example 1. Results are shown in TABLE 2.

Example 34

A Simazine 900g/kg WP formulation of the following composition was prepared by blending the following :

Simazine tech. (98% w/w)	91.8	% w/w
ATPLUS G 73050 (now sold under the trade mark TERSPERSE 3050 by Orica Australia Pty Ltd)	1.7	
DISPERSANT	3.1	
Kaolin	3.4	

where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadine and maleic anhydride. Results are shown in TABLE 3. The wettability of the WP was also measured according to CIPAC test MT 53.5.1.

Example 35

A Simazine 900g/kg WP formulation of the following composition was prepared and tested in the manner described in example 34 where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadiene and maleic anhydride used at 3.1% w/w, the wetting agent was the sodium salt dicyclohexylsulphosuccinate used at 1.7% w/w. Results are shown in TABLE 3.

Example 36

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 34 excepting that the wetting agent used was ECOTERIC AS 20 (Orica Australia Pty Ltd), an alkylpolysaccharide used at 1.7% w/w on an active basis (the product is a 50% solution in water). The results are shown in TABLE 3.

Example 37

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 34 excepting that the wetting agent used was TERIC 157 (Orica Australia Pty Ltd) a nonionic wetter loaded onto an insoluble porous carrier used at 1.7% w/w. The results are shown in TABLE 3.

Example 38

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
WETTER	1.5

Atrazine tech. 97% w/w	51.5 % w/v
Monoethylene glycol	4.0
ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Orica Australia Pty Ltd)	3
DISPERSANT	2
Silicone antifoam	0.2
Rhodopol 23 (Rhodia Inc)	0.2
Proxel GXL 20 (Zeneca plc)	0.1
Water	55.0

The dispersant used was the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride. The SC was prepared by dissolving the monoethylene glycol, ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Orica Australia Pty Ltd) and DISPERSANT in 85% of the water and adding the Atrazine tech. and antifoam with vigorous mixing to form a slurry or millbase premix. The premix is then milled using a Dynomill laboratory scale bead mill to give a suitable particle size distribution of >98% of particles below 5 microns. The millbase thus obtained was then blended with Proxel GXL 20 (Zeneca plc) and Rodopol 23 (Rhodia Inc) in a premix and then made up to the desired volume with the remaining water and mixed to a homogeneous mixture. The SC thus obtained was of usable viscosity and was found to be storage stable after storage at 2 degrees C and 50 degrees C for one month, with minimal syneresis and thickening and no claying,

sedimentation or aggregates being observed.

Example 42

It was attempted to make an SC formulation according to the formula and method of example 41 with 4% w/w of the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride and only 1% w/w ATLOX 4896A (now sold under the trade maek TERSPERSE 4896, Orica Australia Pty Ltd) being used. The resulting millbase premix was of a viscosity which would not allow it to be milled.

CLAIMS

1. A method of dispersing an insoluble material in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium.

2. A method according to claim 1 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

3. A method according to claim 1 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

4. A method according to claim 1 wherein the alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

5. A method according to claim 1 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids, esters and amides, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

6. A method according to claim 1 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, cyclic olefins, both exocyclic and endocyclic, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

7. A method of treatment of a substrate with a insoluble material comprising the following steps:

(i) preparing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an

alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

(ii) dispersing said formulation in an aqueous medium; and

(iii) applying the dispersed formulation to a substrate.

8. An agricultural formulation according to claim 7 wherein the formulation is in the form of a suspension concentrate (SC), a wettable powder (WP) or a water dispersible granule (WG).

9. A method according to claim 7 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

10. A method according to claim 7 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

11. A method according to claim 7 wherein the alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

12. A method according to claim 7 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids, esters and amides, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

13. A method according to claim 7 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, cyclic olefins, both exocyclic and endocyclic, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

14. An agricultural formulation according to claim 7 wherein the dispersant is readily soluble in water.

15. An agricultural formulation according to claim 7 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

16. An agricultural formulation according to claim 7 wherein the alternating copolymer is polyanionic.

17. An agricultural formulation according to claim 7 wherein the alternating copolymer is in the form of its free acid.

18. An agricultural formulation according to claim 7 wherein the dispersant is a water-soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

19. An agricultural formulation according to claim 7 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

20. An agricultural formulation according to claim 5 wherein alternating copolymers are in the range of from 1000 to 30000 daltons.

21. An agricultural formulation according to claim 5 wherein alternating copolymers are in the range of from 1000 to 10000 daltons.

22. An agricultural formulation according to claim 7 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides, algaicides, plant growth regulators, anthelmintics, rodenticides,

nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners, fillers and carriers and other adjuvants.

23. An agricultural formulation according to claim 7 wherein the formulation further comprises a surfactant wetting agent.

24. A method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

25. A method according to claim 24 comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second

comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

(iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

26. A method according to claim 24 comprising the steps of:

(i) combining at least one insoluble material, with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

27. A method according to claim 24 comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β- unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

28. A method according to claim 24 comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises

olefinic compounds containing one or more polymerizable double bonds;

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

29. A method according to claim 24 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

30. A method according to claim 24 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

31. A method according to claim 24 wherein alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

32. A method according to claim 24 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters

amides and imides derived from them, acrylic and methacrylic acids, esters and amides, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

33. A method according to claim 24 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, cyclic olefins, both exocyclic and endocyclic, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

34. An agricultural formulation according to claim 24 wherein the dispersant is readily soluble in water.

35. An agricultural formulation according to claim 24 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

36. An agricultural formulation according to claim 24 wherein the alternating copolymer is polyanionic.

37. An agricultural formulation according to claim 24 wherein the alternating copolymer is in the form of its free acid.

38. An agricultural formulation according to claim 24 wherein the dispersant is a water-soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

39. An agricultural formulation according to claim 24 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

40. An agricultural formulation according to claim 24 wherein alternating copolymers are in the range of from 1000 to 30000 daltons.

41. An agricultural formulation according to claim 24 wherein alternating copolymers are in the range of from 1000 to 10000 daltons.

42. An agricultural formulation according to claim 24 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides, algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners fillers and carriers and other adjuvants.

43. An agricultural formulation according to claim 24 wherein the formulation further comprises a surfactant wetting agent.

44. A method according to any one of claims 26 to 28 wherein said dispersant achieves a percentage suspensibility of greater than 80%.

45. A method according to claim 25 wherein said dispersant achieves a percentage suspensibility of greater than 90%.

46. A method according to either claim 26 or claim 27 wherein the milling step produces an average particle size in the range of from 5 to 15μm.

47. A method according to claim 46 wherein the wettable powder has a wettability of less than 1 minute and a suspensibility above 80%.

48. A method according to claim 28 wherein the milling step produces an average particle size in the range of from 5 to 15μm.

49. A method according to claim 28 wherein the formulation has a dispersion time of less than 1 minute.

50. A method according to claim 28 wherein the formulation has a dispersion time of less than 20 seconds.

51. A method according to claim 28 wherein the formulation has a suspensibility of above 80%.

52. A method according to claim 28 wherein the formulation has a wet sieve retention for a 150 μm sieve of less than 0.1% retained material and for a 53 μm sieve of less than 0.6%.

53. A method according to claim 25 wherein the milling step produces a mean particle size of less than 5μm.

54. A method according to claim 25 wherein the milling step produces a mean particle size in the range of from 1 to 3 μm.

55. An agricultural formulation produced by the method of any one of claims 25 to 28.

56. A method of treatment of a substrate with a insoluble material comprising the following steps:

(i) preparing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

(ii) dispersing said formulation in an aqueous medium; and

(iii) applying the dispersed formulation to a substrate.

57. A method according to claim 56 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

58. A method according to claim 56 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

59. A method according to claim 56 wherein alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

60. A method according to claim 56 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids, esters and amides, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

61. A method according to claim 56 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, cyclic olefins, both exocyclic and endocyclic, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

62. An agricultural formulation according to claim 56 wherein the dispersant is readily soluble in water.

63. An agricultural formulation according to claim 56 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

64. An agricultural formulation according to claim 56 wherein the alternating copolymer is polyanionic.

65. An agricultural formulation according to claim 56 wherein the alternating copolymer is in the form of its free acid.

66. An agricultural formulation according to claim 56 wherein the dispersant is a water-soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

67. An agricultural formulation according to claim 56 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

68. An agricultural formulation according to claim 56 wherein alternating copolymers are in the range of from 1000 to 30000 daltons.

69. An agricultural formulation according to claim 56 wherein alternating copolymers are in the range of from 1000 to 10000 daltons.

70. An agricultural formulation according to claim 56 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides, algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners fillers and carriers and other adjuvants.

71. An agricultural formulation according to claim 56 wherein the formulation further comprises a surfactant wetting agent.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2112337/MJC/RR	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International application No. PCT/AU 98/00854	International filing date *(day/month/year)* 14 October 1998	Priority Date *(day/month/year)* 14 October 1997
International Patent Classification (IPC) or national classification and IPC **Int. Cl.**[6] A01N 25/30, B01F 17/52		
Applicant HUNTSMAN SURFACTANTS TECHNOLOGY CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 29 sheet(s).

3. This report contains indications relating to the following items:

I	[X]	Basis of the report
II	[ ]	Priority
III	[ ]	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	[ ]	Lack of unity of invention
V	[X]	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	[ ]	Certain documents cited
VII	[ ]	Certain defects in the international application
VIII	[ ]	Certain observations on the international application

Date of submission of the demand 14 May 1999	Date of completion of the report 17 September 1999
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. (02) 6285 3929	Authorized Officer GAYE HOROBIN Telephone No. (02) 6283 2069

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

national application No.
PCT/AU 98/00854

I. Basis of the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed.

☒ the description, pages **1-3, 9-22, 29, 30, 33, 34, 37, 40-46,** as originally filed,
pages , filed with the demand,
pages **4-8,23, 26-28, 31,32, 35, 36, 38, 39 ,60,** filed with the letter of **2 September 1999.**

☒ the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages **47-59,** filed with the letter of **2 September 1999.**

☐ the drawings, pages , as originally filed,
pages , filed with the demand,
pages , filed with the letter of .

☐ the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , filed with the letter of .

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, was on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages

☐ the claims, Nos.

☐ the drawings, sheets/fig.

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report*

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-51	YES
	Claims	NO
Inventive step (IS)	Claims 1-51	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-51	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

NOVELTY(N), INVENTIVE STEP(IS)

No citation or obvious combination of citations discloses the features of the claimed invention. The nearest art is considered to be FR 2545325, which discloses an agrochemical wettable granule composition containing a copolymer of maleic anhydride and di-isobutylene. It is disclosed that these two monomers almost inevitably form an alternating copolymer.

separate the active material in the presence of a salt of an acidic resin, such as, for example, a copolymer of maleic anhydride and an α-olefinic compound; add an organic solvent which forms, together with the aqueous medium, a two-phase system; treat such two-phase system by adding a carrier substance thereto; and then isolate the product by a reduction in the volume of the organic phase by the addition of water, the solvent gradually transferring into the added water.

We have now found that the use of a range of derivatisations of alternating copolymers of an α,β-unsaturated oxyacid and an olefin having one or more polymerizable double bonds provides improved dispersibilty and suspensibility in agrochemical formulations, compared to those dispersants already described in the prior art, as well as a number of other ancillary benefits which will be more fully described herein.

According to a first aspect of the present invention, there is provided a method of dispersing an active water-insoluble agrochemical principal in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic

compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) dispersing said formulation in an aqueous medium.

According to a second aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

(iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

According to a third aspect of the present invention, there is provided a method of making

an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

According to a fourth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic

compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

According to a fifth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

According to a sixth aspect of the present invention, there is provided a formulation produced by the process of the second, third, fourth and fifth aspects.

According to a seventh aspect of the present invention, there is provided an agricultural formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

According to an eighth aspect of the present invention, there is provided a method of treatment of a substrate with an active water-insoluble agrochemical principal comprising the following steps:

(i) preparing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) dispersing said formulation in an aqueous medium; and

as obtained from ECOTERIC AS 20 and ECOTERIC AS10 (Huntsman Corporation Australia Pty Ltd). Most preferred from the monoalkylsulphosuccinate class are sodium or potassium salts of cyclohexyl, iso-octyl and n-octyl sulphosuccinate. Most preferred from the dialkylsulphosuccinate class are sodium or potassium salts of dicyclohexyl, diisooctyl and di-n-octyl sulphosuccinates. Most preferred from the class of nonionic surfactants loaded onto insoluble porous silicate carriers are ethoxylated surfactants loaded onto carriers such as TERIC 157 (Huntsman Corporation Australia Pty Ltd). Most preferred wetting agents from the urea surfactant complexes are urea adducts of alcohol ethoxylate surfactants such as TERWET 7050 (Huntsman Corporation Australia Pty Ltd). The wetters herein described show good wettability and dispersibility for the formulations and have the additional advantage of showing storage stability in combination with the copolymer dispersants described. Whereas by comparison some commonly used WG and WP wetters such as alkylnaphthalene sulphonate salts and lignosulphonate salts have been found to show poor storage stability.

In the case of SC formulations in the present invention an active ingredient is typically added to water containing a dispersant, preferably with a surfactant wetting agent together with a conventional non-ionic dispersant. A humectant may also be included. A dispersion is formed using high shear mixing. The dispersion is then milled by any one of several means of wet milling so that the mean particle size of the dispersed solid is below 5 μm more typically in the range of from 1 to 3μm. The resulting product is known as a millbase and may be modified with additives such as antifreeze, thickeners and antisettling agents, biocides and colouring agents may be added. For an SC formulation to be acceptable it should not

Example 3.

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of an alternating copolymer of n-octene and maleic anhydride of approximate molecular weight 20,000 to 30,000. The granules were prepared and tested in the manner described in Example 1. The results are shown in TABLE 1.

Example 4.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a copolymer of n-decene and maleic anhydride. Results are shown in TABLE 1.

Example 5.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a copolymer of diisobutylene and maleic anhydride of approximate molecular weight 30,000 to 40,000. Results are shown in TABLE 1.

Example 6.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 1000 (Atochem Inc.) which is a 1:1 molar ratio copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

Example 7.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 3000 (Atochem Inc.) which is a 3:1 molar ratio copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

Example 8.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of GANTREZ AN 119 resin (Rhodia Inc.) which is a copolymer of methylvinyl ether and maleic anhydride. Results are shown in TABLE 1.

Example 9.

A Simazine 900g/kg WG formulation of the following composition was prepared.

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	6.2
Water	0.5%

The dispersant used was the monoammonium salt of an alternating copolymer of diisobutylene

and maleic anhydride. The granules were prepared and tested in the manner described in Example 1. Results are shown in TABLE 1.

Example 10

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of an alternating copolymer of undecylenic acid and maleic anhydride. The granules were prepared and tested in the manner described in example1. Results are shown in TABLE 2.

Example 11

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating copolymer of vinyl isobutyl ether and maleic anhydride. Results are shown in TABLE 2.

Example 12

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating copolymer of

ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in Example 1. Results are shown in TABLE 2.

Example 22

An Atrazine 900g/kg WG formulation was prepared and tested in the manner described in Example 21 with the dispersant being the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 23

A Diuron 900g/kg WG formulation of the following composition was prepared.

Diuron tech. (97% w/w)	92.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 3050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	2.1
Water	0.5

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in example 1. Results are shown in TABLE 2.

Example 24

A Diuron 900g/kg WG formulation was prepared and tested in the manner described in example 23 with the dispersant being the sodium salt of an alternating co-polymer of alphamethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 25

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of a terpolymer not of alternating character between comonomers of first and second type comprising alphamethylstyrene, styrene and maleic anhydride. The granules were prepared and tested in the manner described in example1. Results are shown in TABLE 2.

Example 26.

ATPLUS G73050 (now sold under the trade mark TERSPERSE 3050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5

with the dispersant being the sodium salt of a terpolymer of alternating character between monomers of first and second type comprising alphamethyl styrene, dicyclopentadiene and maleic anhydride. The granules were made and tested as described in Example 1. Results are shown in TABLE 2.

Example 34

A Simazine 900g/kg WP formulation of the following composition was prepared by blending the following :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G 73050 (now sold under the trade mark TERSPERSE 3050 by Huntsman Corporation Australia Pty Ltd)	1.7
DISPERSANT	3.1
Kaolin	3.4

where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadine and maleic anhydride. Results are shown in TABLE 3. The wettability of the WP was also measured according to CIPAC test MT 53.5.1.

Example 35

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A Simazine 900g/kg WP formulation of the following composition was prepared and tested in the manner described in example 34 where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadiene and maleic anhydride used at 3.1% w/w, the wetting agent was the sodium salt dicyclohexylsulphosuccinate used at 1.7% w/w. Results are shown in TABLE 3.

Example 36

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 34 excepting that the wetting agent used was ECOTERIC AS 20 (Huntsman Corporation Australia Pty Ltd), an alkylpolysaccharide used at 1.7% w/w on an active basis (the product is a 50% solution in water). The results are shown in TABLE 3.

Example 37

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 34 excepting that the wetting agent used was TERIC 157 (Huntsman Corporation Australia Pty Ltd) a nonionic wetter loaded onto an insoluble porous carrier used at 1.7% w/w. The results are shown in TABLE 3.

Example 38

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
WETTER	1.5

Monoethylene glycol	4.0
ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Huntsman Corporation Australia Pty Ltd)	3
DISPERSANT	2
Silicone antifoam	0.2
Rhodopol 23 (Rhodia Inc)	0.2
Proxel GXL 20 (Zeneca plc)	0.1
Water	55.0

The dispersant used was the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride. The SC was prepared by dissolving the monoethylene glycol, ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Huntsman Corporation Australia Pty Ltd) and DISPERSANT in 85% of the water and adding the Atrazine tech. and antifoam with vigorous mixing to form a slurry or millbase premix. The premix is then milled using a Dynomill laboratory scale bead mill to give a suitable particle size distribution of >98% of particles below 5 microns. The millbase thus obtained was then blended with Proxel GXL 20 (Zeneca plc) and Rodopol 23 (Rhodia Inc) in a premix and then made up to the desired volume with the remaining water and mixed to a homogeneous mixture. The SC thus obtained was of usable viscosity and was found to be storage stable after storage at 2 degrees C and 50 degrees C for one month, with minimal syneresis and thickening and no claying,

sedimentation or aggregates being observed.

Example 42

It was attempted to make an SC formulation according to the formula and method of example 41 with 4% w/w of the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride and only 1% w/w ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Huntsman Corporation Australia Pty Ltd) being used. The resulting millbase premix was of a viscosity which would not allow it to be milled.

CLAIMS

1. A method of dispersing an active water-insoluble agrochemical principal in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium;

with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

2. A method according to claim 1 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

3. A method according to claim 1 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

4. A method according to claim 1 wherein the alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

5. A method according to claim 1 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids and the corresponding esters and amides derived from them, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

6. A method according to claim 1 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, exocyclic and endocyclic olefins, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

7. An agricultural formulation comprising at least one insoluble material and at least

one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

8. An agricultural formulation according to claim 7 wherein the formulation is in the form of a suspension concentrate (SC), a wettable powder (WP) or a water dispersible granule (WG).

9. An agricultural formulation according to claim 7 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

10. An agricultural formulation according to claim 7 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

11. An agricultural formulation according to claim 7 wherein the alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

12. An agricultural formulation according to claim 7 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids and the esters and amides derived from them, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

13. An agricultural formulation according to claim 7 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, exocyclic and endocyclic olefins, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

14. An agricultural formulation according to claim 7 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

15. An agricultural formulation according to claim 7 wherein the alternating copolymer is in the form of its free acid.

16. An agricultural formulation according to claim 7 wherein the dispersant is a water-soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

17. An agricultural formulation according to claim 7 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

18. An agricultural formulation according to claim 7 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides, algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners, fillers and carriers and other adjuvants.

19. An agricultural formulation according to claim 7 wherein the formulation further comprises a surfactant wetting agent.

20. An agricultural formulation according to claim 19 wherein the surfactant wetting agent is selected from the group consisting of an alkylpolysaccharide; di or mono alkyl sulphosuccinate derivative; a nonionic surfactant loaded onto an inert silicate carrier; and a non-ionic surfactant delivered in the form of a urea surfactant complex.

21. A method of making an agrochemical formulation comprising the step of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

22. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

(iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

23. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material, with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

24. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at

least one residue of a second comonomer, wherein said first comonomer comprises α,β- unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

25. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

26. A method according to claim 21 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

27. A method according to claim 21 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

28. A method according to claim 21 wherein alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

29. A method according to claim 21 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids and the corresponding esters and amides derived from them, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

30. A method according to claim 21 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, exocyclic and endocyclic olefins, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

31. A method according to claim 21 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

32. A method according to claim 21 wherein the alternating copolymer is in the form of its free acid.

33. A method according to claim 21 wherein the dispersant is a water- soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

34. A method according to claim 21 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

35. A method according to claim 21 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides,

algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners, fillers and carriers and other adjuvants.

36. A method according to claim 21 wherein the formulation further comprises a surfactant wetting agent.

37. A method according to claim 36 wherein the surfactant wetting agent is selected from the group consisting of an alkylpolysaccharide; di or mono alkyl sulphosuccinate derivative; a nonionic surfactant loaded onto an inert silicate carrier; and a non-ionic surfactant delivered in the form of a urea surfactant complex.

38. A method according to any one of claims 23 to 25 wherein said dispersant achieves a percentage suspensibility of greater than 80%.

39. A method according to claim 22 wherein said dispersant achieves a percentage suspensibility of greater than 90%.

40. A method according to either claim 23 or claim 24 wherein the milling step produces an average particle size in the range of from 5 to 15μm.

41. A method according to claim 25 wherein the milling step produces an average particle size in the range of from 5 to 15μm.

42. A method according to claim 25 wherein the formulation has a dispersion time of less than 1 minute.

43. A method according to claim 25 wherein the formulation has a dispersion time of less than 20 seconds.

44. A method according to claim 25 wherein the formulation has a wet sieve retention for a 150 μm sieve of less than 0.1% retained material and for a 53 μm sieve of less than 0.6%.

45. A method according to claim 22 wherein the milling step produces a mean particle size of less than 5µm.

46. A method according to claim 22 wherein the milling step produces a mean particle size in the range of from 1 to 3 µm.

47. An agricultural formulation produced by the method of any one of claims 22 to 25.

48. A method of treatment of a substrate with an active water-insoluble agrochemical principal comprising the following steps:

(i) preparing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble

agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) dispersing said formulation in an aqueous medium; and

(iii) applying the dispersed formulation to a substrate.

49. A method according to claim 48 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

50. A method according to claim 48 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

51. A method according to claim 48 wherein alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

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ABSTRACT

A method of dispersing an insoluble material in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises αβ-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium.

PATENT COOPERATION TREATY

PCT

CORRECTED VERSION

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2112337/MJC/RR	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International application No. PCT/AU 98/00854	International filing date *(day/month/year)* 14 October 1998	Priority Date *(day/month/year)* 14 October 1997
International Patent Classification (IPC) or national classification and IPC Int. Cl.[6] A01N 25/30, B01F 17/52		
Applicant HUNTSMAN SURFACTANTS TECHNOLOGY CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 29 sheet(s).

3. This report contains indications relating to the following items:

I	[X]	Basis of the report
II	[ ]	Priority
III	[ ]	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	[ ]	Lack of unity of invention
V	[X]	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	[ ]	Certain documents cited
VII	[ ]	Certain defects in the international application
VIII	[ ]	Certain observations on the international application

Date of submission of the demand 14 May 1999	Date of completion of the report 17 September 1999
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. (02) 6285 3929	Authorized Officer GAYE HOROBIN Telephone No. (02) 6283 2069

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/AU 98/00854

I. Basis of the report

1. With regard to the **elements** of the international application:*

[ ] the international application as originally filed.

[X] the description, pages **1-3, 9-22, 24, 25, 29, 30, 33, 34, 37, 40-46,** as originally filed,
pages , filed with the demand,
pages **4-8,23, 26-28, 31,32, 35, 36, 38, 39 ,60,** filed with the letter of **2 September 1999**.

[X] the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages **47-59,** filed with the letter of **2 September 1999**.

[ ] the drawings, pages , as originally filed,
pages , filed with the demand,
pages , filed with the letter of .

[ ] the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , filed with the letter of .

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language which is:

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application (under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, was on the basis of the sequence listing:

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. [ ] The amendments have resulted in the cancellation of:

[ ] the description, pages
[ ] the claims, Nos.
[ ] the drawings, sheets/fig.

5. [ ] This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/AU 98/00854

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-51	YES
	Claims	NO
Inventive step (IS)	Claims 1-51	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-51	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

NOVELTY(N), INVENTIVE STEP(IS)
No citation or obvious combination of citations discloses the features of the claimed invention. The nearest art is considered to be FR 2545325, which discloses an agrochemical wettable granule composition containing a copolymer of maleic anhydride and di-isobutylene. It is disclosed that these two monomers almost inevitably form an alternating copolymer.

separate the active material in the presence of a salt of an acidic resin, such as, for example, a copolymer of maleic anhydride and an α-olefinic compound; add an organic solvent which forms, together with the aqueous medium, a two-phase system; treat such two-phase system by adding a carrier substance thereto; and then isolate the product by a reduction in the volume of the organic phase by the addition of water, the solvent gradually transferring into the added water.

We have now found that the use of a range of derivatisations of alternating copolymers of an α,β-unsaturated oxyacid and an olefin having one or more polymerizable double bonds provides improved dispersibilty and suspensibility in agrochemical formulations, compared to those dispersants already described in the prior art, as well as a number of other ancillary benefits which will be more fully described herein.

According to a first aspect of the present invention, there is provided a method of dispersing an active water-insoluble agrochemical principal in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic

compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) dispersing said formulation in an aqueous medium.

According to a second aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

(iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

According to a third aspect of the present invention, there is provided a method of making

an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

According to a fourth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic

compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

According to a fifth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

According to a sixth aspect of the present invention, there is provided a formulation produced by the process of the second, third, fourth and fifth aspects.

According to a seventh aspect of the present invention, there is provided an agricultural formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

According to an eighth aspect of the present invention, there is provided a method of treatment of a substrate with an active water-insoluble agrochemical principal comprising the following steps:

(i) preparing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) dispersing said formulation in an aqueous medium; and

as obtained from ECOTERIC AS 20 and ECOTERIC AS10 (Huntsman Corporation Australia Pty Ltd). Most preferred from the monoalkylsulphosuccinate class are sodium or potassium salts of cyclohexyl, iso-octyl and n-octyl sulphosuccinate. Most preferred from the dialkylsulphosuccinate class are sodium or potassium salts of dicyclohexyl, diisooctyl and di-n-octyl sulphosuccinates. Most preferred from the class of nonionic surfactants loaded onto insoluble porous silicate carriers are ethoxylated surfactants loaded onto carriers such as TERIC 157 (Huntsman Corporation Australia Pty Ltd). Most preferred wetting agents from the urea surfactant complexes are urea adducts of alcohol ethoxylate surfactants such as TERWET 7050 (Huntsman Corporation Australia Pty Ltd). The wetters herein described show good wettability and dispersibility for the formulations and have the additional advantage of showing storage stability in combination with the copolymer dispersants described. Whereas by comparison some commonly used WG and WP wetters such as alkylnaphthalene sulphonate salts and lignosulphonate salts have been found to show poor storage stability.

In the case of SC formulations in the present invention an active ingredient is typically added to water containing a dispersant, preferably with a surfactant wetting agent together with a conventional non-ionic dispersant. A humectant may also be included. A dispersion is formed using high shear mixing. The dispersion is then milled by any one of several means of wet milling so that the mean particle size of the dispersed solid is below 5 μm more typically in the range of from 1 to 3μm. The resulting product is known as a millbase and may be modified with additives such as antifreeze, thickeners and antisettling agents, biocides and colouring agents may be added. For an SC formulation to be acceptable it should not

Example 3.

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of an alternating copolymer of n-octene and maleic anhydride of approximate molecular weight 20,000 to 30,000. The granules were prepared and tested in the manner described in Example 1. The results are shown in TABLE 1.

Example 4.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a copolymer of n-decene and maleic anhydride. Results are shown in TABLE 1.

Example 5.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a copolymer of diisobutylene and maleic anhydride of approximate molecular weight 30,000 to 40,000. Results are shown in TABLE 1.

Example 6.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 1000 (Atochem Inc.) which is a 1:1 molar ratio copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

Example 7.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 3000 (Atochem Inc.) which is a 3:1 molar ratio copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

Example 8.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of GANTREZ AN 119 resin (Rhodia Inc.) which is a copolymer of methylvinyl ether and maleic anhydride. Results are shown in TABLE 1.

Example 9.

A Simazine 900g/kg WG formulation of the following composition was prepared.

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	6.2
Water	0.5%

The dispersant used was the monoammonium salt of an alternating copolymer of diisobutylene

and maleic anhydride. The granules were prepared and tested in the manner described in Example 1. Results are shown in TABLE 1.

Example 10

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of an alternating copolymer of undecylenic acid and maleic anhydride. The granules were prepared and tested in the manner described in example1. Results are shown in TABLE 2.

Example 11

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating copolymer of vinyl isobutyl ether and maleic anhydride. Results are shown in TABLE 2.

Example 12

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating copolymer of

ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in Example 1. Results are shown in TABLE 2.

Example 22

An Atrazine 900g/kg WG formulation was prepared and tested in the manner described in Example 21 with the dispersant being the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 23

A Diuron 900g/kg WG formulation of the following composition was prepared.

Diuron tech. (97% w/w)	92.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 3050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	2.1
Water	0.5

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in example 1. Results are shown in TABLE 2.

Example 24

A Diuron 900g/kg WG formulation was prepared and tested in the manner described in example 23 with the dispersant being the sodium salt of an alternating co-polymer of alphamethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 25

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G73050 (now sold under the trade mark TERSPERSE 7050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5%

The dispersant used was the sodium salt of a terpolymer not of alternating character between comonomers of first and second type comprising alphamethylstyrene, styrene and maleic anhydride. The granules were prepared and tested in the manner described in example1. Results are shown in TABLE 2.

Example 26.

ATPLUS G73050 (now sold under the trade mark TERSPERSE 3050 by Huntsman Corporation Australia Pty Ltd)	1.5
DISPERSANT	3.1
Kaolin	3.1
Water	0.5

with the dispersant being the sodium salt of a terpolymer of alternating character between monomers of first and second type comprising alphamethyl styrene, dicyclopentadiene and maleic anhydride. The granules were made and tested as described in Example 1. Results are shown in TABLE 2.

Example 34

A Simazine 900g/kg WP formulation of the following composition was prepared by blending the following :

Simazine tech. (98% w/w)	91.8 % w/w
ATPLUS G 73050 (now sold under the trade mark TERSPERSE 3050 by Huntsman Corporation Australia Pty Ltd)	1.7
DISPERSANT	3.1
Kaolin	3.4

where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadine and maleic anhydride. Results are shown in TABLE 3. The wettability of the WP was also measured according to CIPAC test MT 53.5.1.

Example 35

A Simazine 900g/kg WP formulation of the following composition was prepared and tested in the manner described in example 34 where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadiene and maleic anhydride used at 3.1% w/w, the wetting agent was the sodium salt dicyclohexylsulphosuccinate used at 1.7% w/w. Results are shown in TABLE 3.

Example 36

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 34 excepting that the wetting agent used was ECOTERIC AS 20 (Huntsman Corporation Australia Pty Ltd), an alkylpolysaccharide used at 1.7% w/w on an active basis (the product is a 50% solution in water). The results are shown in TABLE 3.

Example 37

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 34 excepting that the wetting agent used was TERIC 157 (Huntsman Corporation Australia Pty Ltd) a nonionic wetter loaded onto an insoluble porous carrier used at 1.7% w/w. The results are shown in TABLE 3.

Example 38

A Simazine 900g/kg WG formulation of the following composition was prepared :

Simazine tech. (98% w/w)	91.8 % w/w
WETTER	1.5

Monoethylene glycol	4.0
ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Huntsman Corporation Australia Pty Ltd)	3
DISPERSANT	2
Silicone antifoam	0.2
Rhodopol 23 (Rhodia Inc)	0.2
Proxel GXL 20 (Zeneca plc)	0.1
Water	55.0

The dispersant used was the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride. The SC was prepared by dissolving the monoethylene glycol, ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Huntsman Corporation Australia Pty Ltd) and DISPERSANT in 85% of the water and adding the Atrazine tech. and antifoam with vigorous mixing to form a slurry or millbase premix. The premix is then milled using a Dynomill laboratory scale bead mill to give a suitable particle size distribution of >98% of particles below 5 microns. The millbase thus obtained was then blended with Proxel GXL 20 (Zeneca plc) and Rodopol 23 (Rhodia Inc) in a premix and then made up to the desired volume with the remaining water and mixed to a homogeneous mixture. The SC thus obtained was of usable viscosity and was found to be storage stable after storage at 2 degrees C and 50 degrees C for one month, with minimal syneresis and thickening and no claying,

sedimentation or aggregates being observed.

Example 42

It was attempted to make an SC formulation according to the formula and method of example 41 with 4% w/w of the sodium salt of an alternating copolymer of alphamethylstyrene and maleic anhydride and only 1% w/w ATLOX 4896A (now sold under the trade mark TERSPERSE 4896, Huntsman Corporation Australia Pty Ltd) being used. The resulting millbase premix was of a viscosity which would not allow it to be milled.

CLAIMS

1. A method of dispersing an active water-insoluble agrochemical principal in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium;

with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

2. A method according to claim 1 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

3. A method according to claim 1 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

4. A method according to claim 1 wherein the alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

5. A method according to claim 1 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids and the corresponding esters and amides derived from them, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

6. A method according to claim 1 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, exocyclic and endocyclic olefins, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

7. An agricultural formulation comprising at least one insoluble material and at least

one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

8. An agricultural formulation according to claim 7 wherein the formulation is in the form of a suspension concentrate (SC), a wettable powder (WP) or a water dispersible granule (WG).

9. An agricultural formulation according to claim 7 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

10. An agricultural formulation according to claim 7 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

11. An agricultural formulation according to claim 7 wherein the alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

12. An agricultural formulation according to claim 7 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids and the esters and amides derived from them, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

13. An agricultural formulation according to claim 7 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, exocyclic and endocyclic olefins, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

14. An agricultural formulation according to claim 7 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

15. An agricultural formulation according to claim 7 wherein the alternating copolymer is in the form of its free acid.

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16. An agricultural formulation according to claim 7 wherein the dispersant is a water-soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

17. An agricultural formulation according to claim 7 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

18. An agricultural formulation according to claim 7 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides, algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners, fillers and carriers and other adjuvants.

19. An agricultural formulation according to claim 7 wherein the formulation further comprises a surfactant wetting agent.

20. An agricultural formulation according to claim 19 wherein the surfactant wetting agent is selected from the group consisting of an alkylpolysaccharide; di or mono alkyl sulphosuccinate derivative; a nonionic surfactant loaded onto an inert silicate carrier; and a non-ionic surfactant delivered in the form of a urea surfactant complex.

21. A method of making an agrochemical formulation comprising the step of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene.

22. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

(iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

23. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material, with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

24. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at

least one residue of a second comonomer, wherein said first comonomer comprises α,β- unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

25. A method according to claim 21 comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

26. A method according to claim 21 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

27. A method according to claim 21 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

28. A method according to claim 21 wherein alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

29. A method according to claim 21 wherein the first comonomer is selected from the group consisting of fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids and the corresponding esters and amides derived from them, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

30. A method according to claim 21 wherein the second comonomer is selected from the group consisting of styrene and its alkyl and halo derivatives, vinyl ethers and esters, α-olefins, internal olefins, exocyclic and endocyclic olefins, allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

31. A method according to claim 21 wherein the dispersant is an agriculturally acceptable salt of the alternating copolymer and wherein the salt comprises sodium, potassium and/or ammonium ions.

32. A method according to claim 21 wherein the alternating copolymer is in the form of its free acid.

33. A method according to claim 21 wherein the dispersant is a water- soluble agriculturally acceptable derivative of the alternating copolymer wherein said derivative is selected from the group consisting of polyalkyleneoxy derivatives, polyethyleneglycol derivatives, polyamide derivatives and polyvinyl alcohol derivatives.

34. A method according to claim 21 wherein alternating copolymers are in the range of from 1000 to 90000 daltons.

35. A method according to claim 21 wherein the water-insoluble materials are selected from the group consisting of herbicides, insecticides, fungicides, biocides, molluscicides,

algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacides, fertilizers, crop safeners, fillers and carriers and other adjuvants.

36. A method according to claim 21 wherein the formulation further comprises a surfactant wetting agent.

37. A method according to claim 36 wherein the surfactant wetting agent is selected from the group consisting of an alkylpolysaccharide; di or mono alkyl sulphosuccinate derivative; a nonionic surfactant loaded onto an inert silicate carrier; and a non-ionic surfactant delivered in the form of a urea surfactant complex.

38. A method according to any one of claims 23 to 25 wherein said dispersant achieves a percentage suspensibility of greater than 80%.

39. A method according to claim 22 wherein said dispersant achieves a percentage suspensibility of greater than 90%.

40. A method according to either claim 23 or claim 24 wherein the milling step produces an average particle size in the range of from 5 to 15μm.

41. A method according to claim 25 wherein the milling step produces an average particle size in the range of from 5 to 15μm.

42. A method according to claim 25 wherein the formulation has a dispersion time of less than 1 minute.

43. A method according to claim 25 wherein the formulation has a dispersion time of less than 20 seconds.

44. A method according to claim 25 wherein the formulation has a wet sieve retention for a 150 μm sieve of less than 0.1% retained material and for a 53 μm sieve of less than 0.6%.

45. A method according to claim 22 wherein the milling step produces a mean particle size of less than 5µm.

46. A method according to claim 22 wherein the milling step produces a mean particle size in the range of from 1 to 3 µm.

47. An agricultural formulation produced by the method of any one of claims 22 to 25.

48. A method of treatment of a substrate with an active water-insoluble agrochemical principal comprising the following steps:

(i) preparing a formulation comprising at least one active water-insoluble agrochemical principal and at least one dispersant comprising a water soluble

agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises α,β-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds, with the proviso that the alternating copolymer is not a copolymer of maleic anhydride and diisobutylene;

(ii) dispersing said formulation in an aqueous medium; and

(iii) applying the dispersed formulation to a substrate.

49. A method according to claim 48 wherein the alternating copolymer has an alternating character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer.

50. A method according to claim 48 wherein the alternating copolymer has an alternating character defined by greater than 90% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer,

51. A method according to claim 48 wherein alternating copolymer contains additional comonomer residues which will not substantially change the alternating character of the copolymer.

ABSTRACT

A method of dispersing an insoluble material in an aqueous solution comprising the following steps:

(i) providing a formulation comprising at least one insoluble material and at least one dispersant comprising a water soluble agriculturally acceptable derivative of an alternating copolymer or an agriculturally acceptable salt thereof wherein said alternating copolymer comprises at least one residue of a first comonomer and at least one residue of a second comonomer, wherein said first comonomer comprises αβ-unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium.